Characteristics of Measurements of Total Carbon in Soil with Laser-Induced Breakdown Spectroscopy (LIBS): Improving Analytical Capabilities

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Costs of Monitoring Terrestrial Sequestration Drives Instrument Development

- **MM&V costs must be < 10% of carbon worth**
- **Carbon analyses must be developed that cost less than current methods and provide improved accuracy and precision**
- **Targets:**

  --- costs less than $10-15

  --- detection limits <1 g-C/kg soil

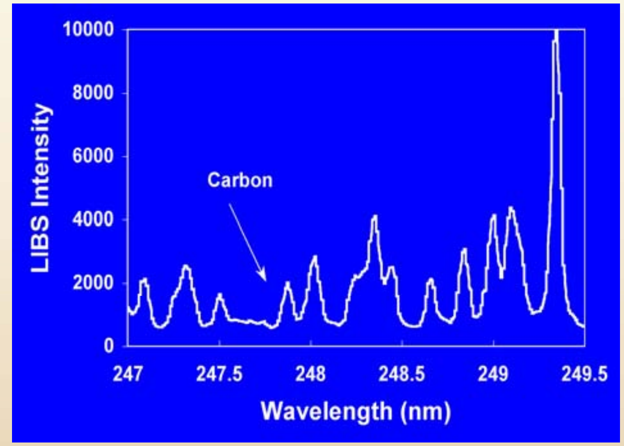
- **Cost of sequestration less than $10 per ton**

➡ **LIBS (laser-induced breakdown spectroscopy) and associated techniques are being developed to meet these requirements**

Laser-Induced Breakdown Spectroscopy

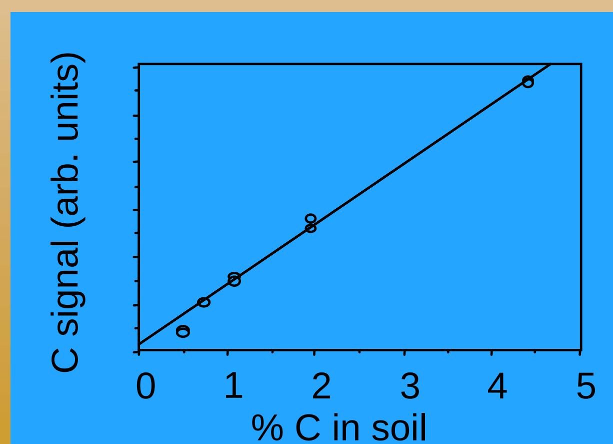
Laser Spark on Soil

- **Nd:YAG laser at 1064 nm**
- **Pulsed at 10Hz**
- **< 1 mm spot size**



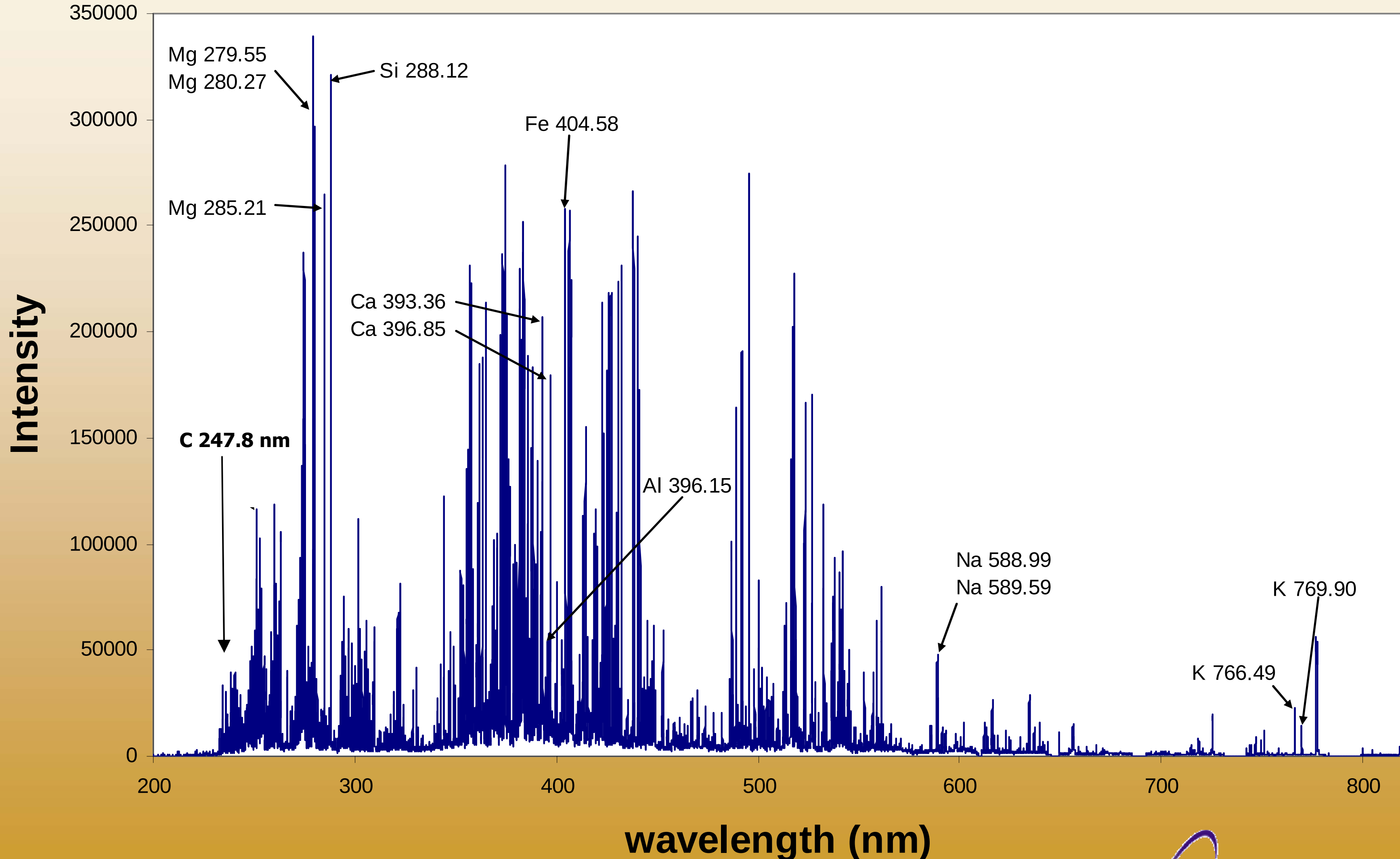
Spectrum from Plasma

- **Interrogates soil using high power laser pulses**
- **Provides information on elemental composition**



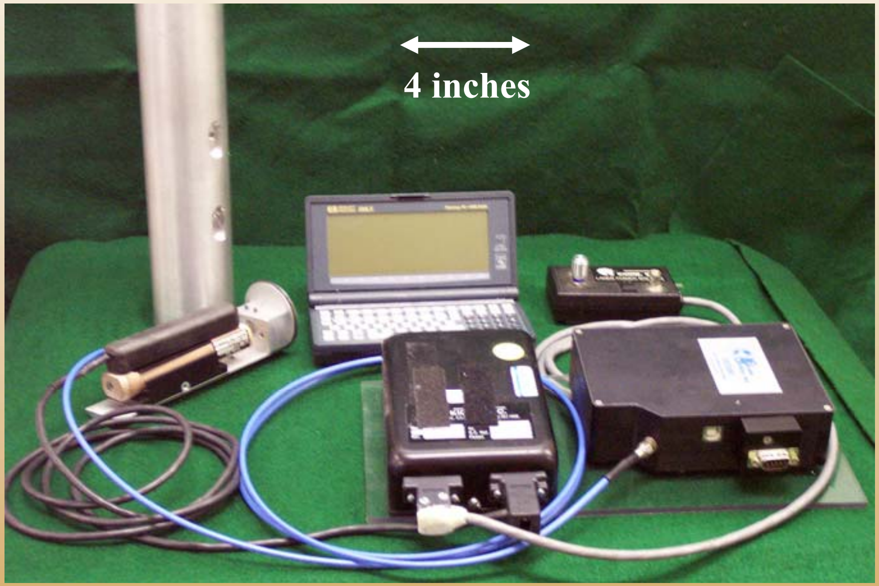
- **Patent in process for technology/instrument**
- **R&D-100 award 2003 for field-deployable instrument**

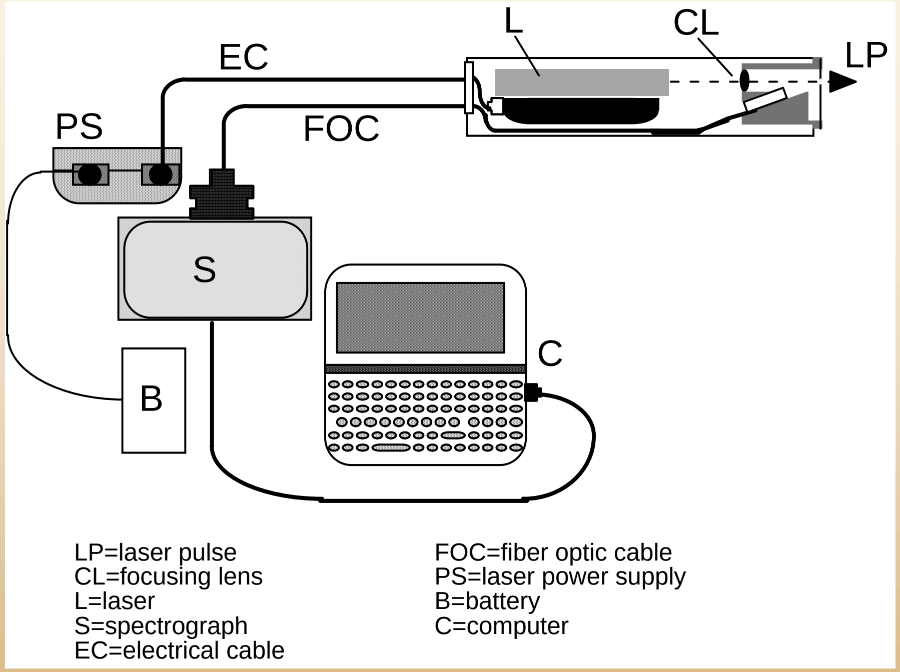
LIBS Spectrum has a High Density of Information



Person-Portable LIBS Instruments Developed

Develop a state-of-the-art LIBS instrument for field determinations of carbon





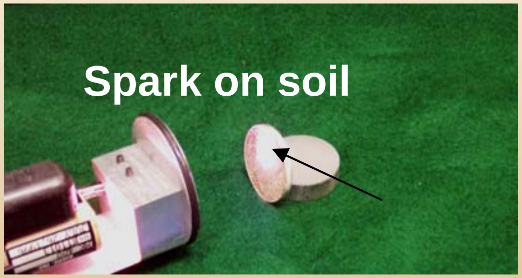
Current Person-Portable LIBS specifications:

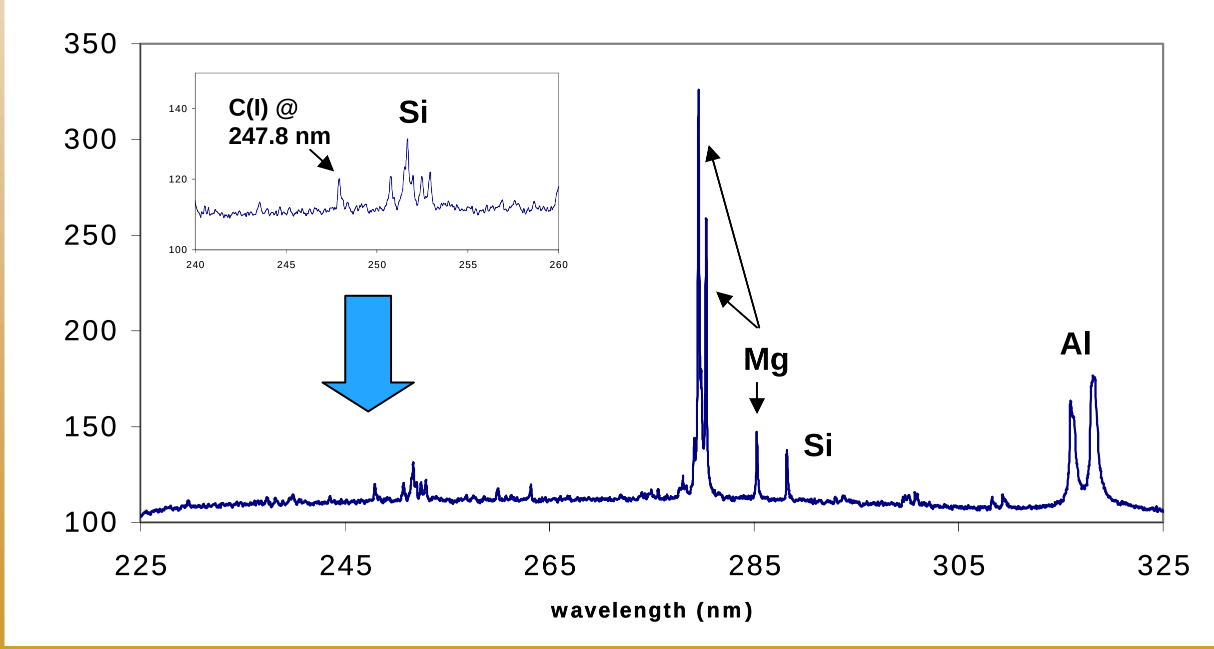
- Wt. = <15 lbs.
- Start up time (limited by computer boot time)
- Projected C detection limit (approx. 500 ppm)
- Rugged components
- Analysis time < 1 minute/sample
- Battery run time (4 hours)

Person-Portable LIBS Instrument

Main Components:

- **Laser - KIGRE MK-367 (Nd:YAG FL-pumped, 1064 nm wavelength)**
- **Spectrograph/detector - Ocean Optics HR2000 with high res. (0.1 nm) at 247.8 nm**
- **Mini-Computer driven**





High quality spectra are obtained with the instrument

Person-Portable LIBS Instrument

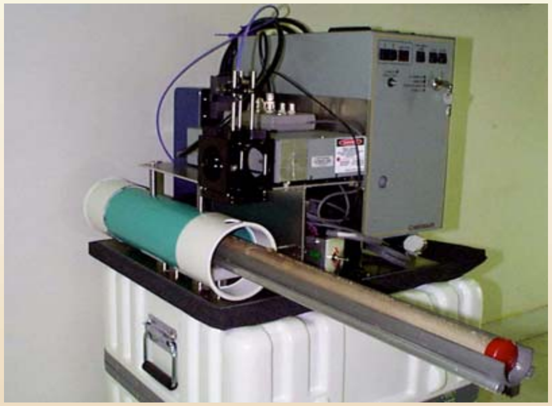
Packaged unit

- **Packaged in small suitcase**
- **Currently operated using laptop computer**
- **Software in development and testing**

Vibration test of HR2000 at LANL

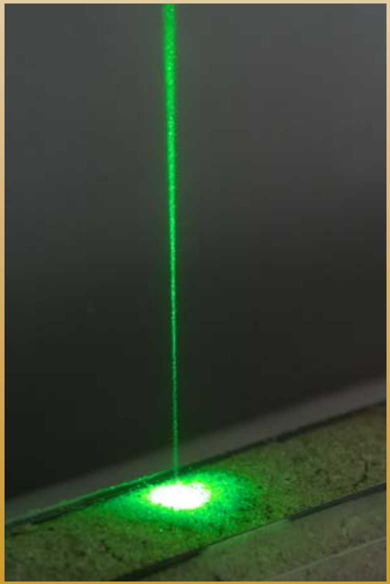
- **Rugged version of HR2000 under development with Ocean Optics (vibration and thermal testing)**
- **Laboratory and field testing of instruments in 2004**

LIBS Field-Deployable Instrument



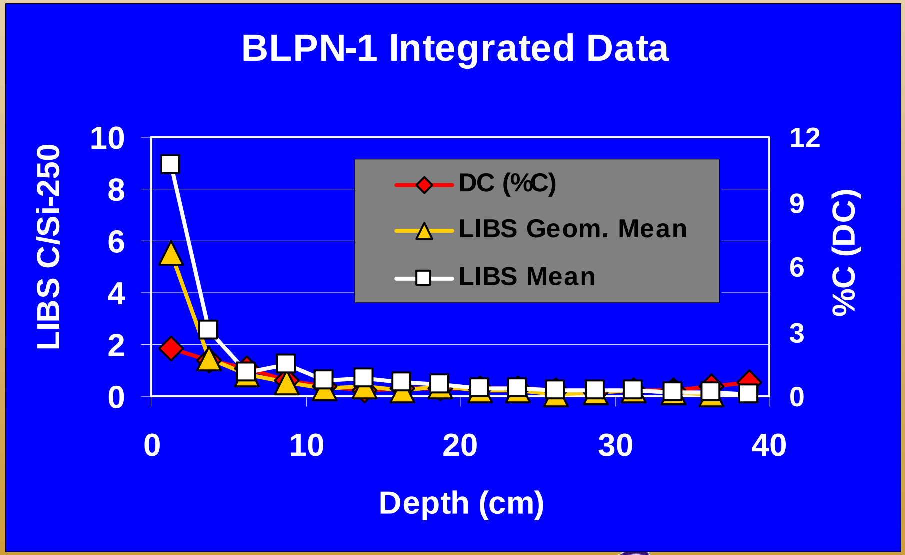
- 10 sec/measurement
- 36 in core in 15 min. (High Res) or 5 min (Low Res)
- monitors all elements in soil

LIBS Core Analysis



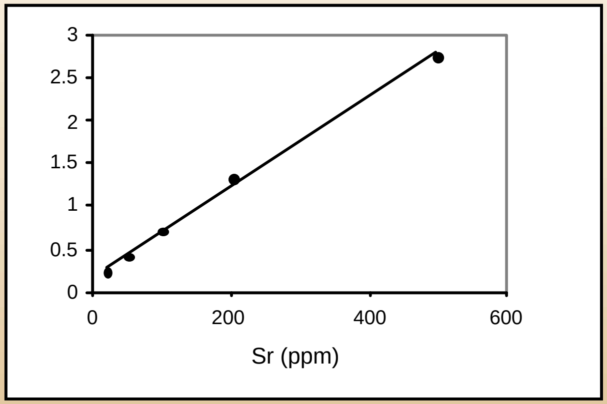
Interrogation of a soil core sample by the LIBS laser beam

Results

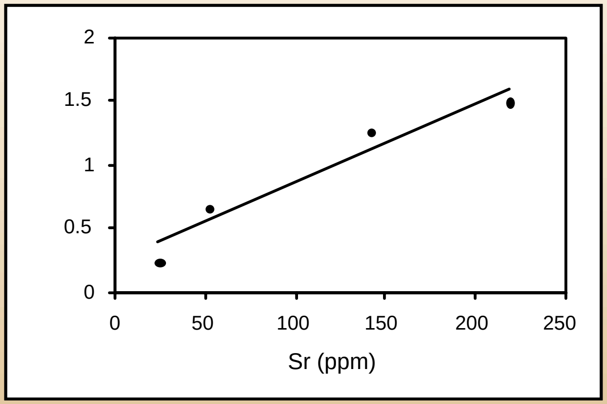


Enhancing LIBS Capabilities via Chemometric Methods

Reduce the effect of matrix composition on carbon calibrations & analysis



Cal. Curve for constant matrix samples

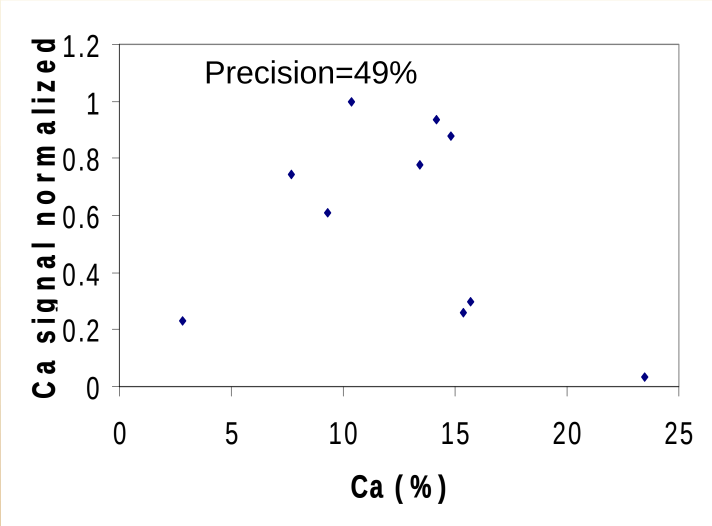


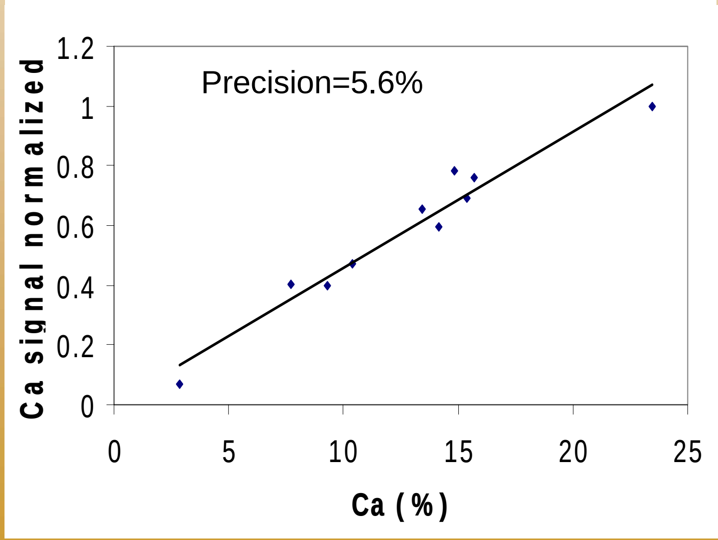
Cal. Curve for soils with different matrices

Changes in the concentrations of major elements (e.g. Si, Al, Ca) may produce matrix effects

- Spectra of certified soil samples (from NRCS) have been obtained and are being evaluated to determine any inter-element correlations.
- Correlations between carbon signals and major elements (e.g. Al, Ca, high and low clay soils) are being evaluated.
- Effects on plasma excitation conditions (e.g. temperature) are being determined.

Minimizing Matrix Effects by New Measurement Procedures





By analyzing the data in certain ways, matrix effects can be greatly reduced. We have developed one method*, (shown at the left) based on experimental procedure rather than chemometrics, that improves analysis results significantly.

Top - Ca cal curve for soils with widely varying matrices (major element concentrations).

Bottom - Same samples analyzed using new procedure that minimizes matrix effects.

***patent disclosure**

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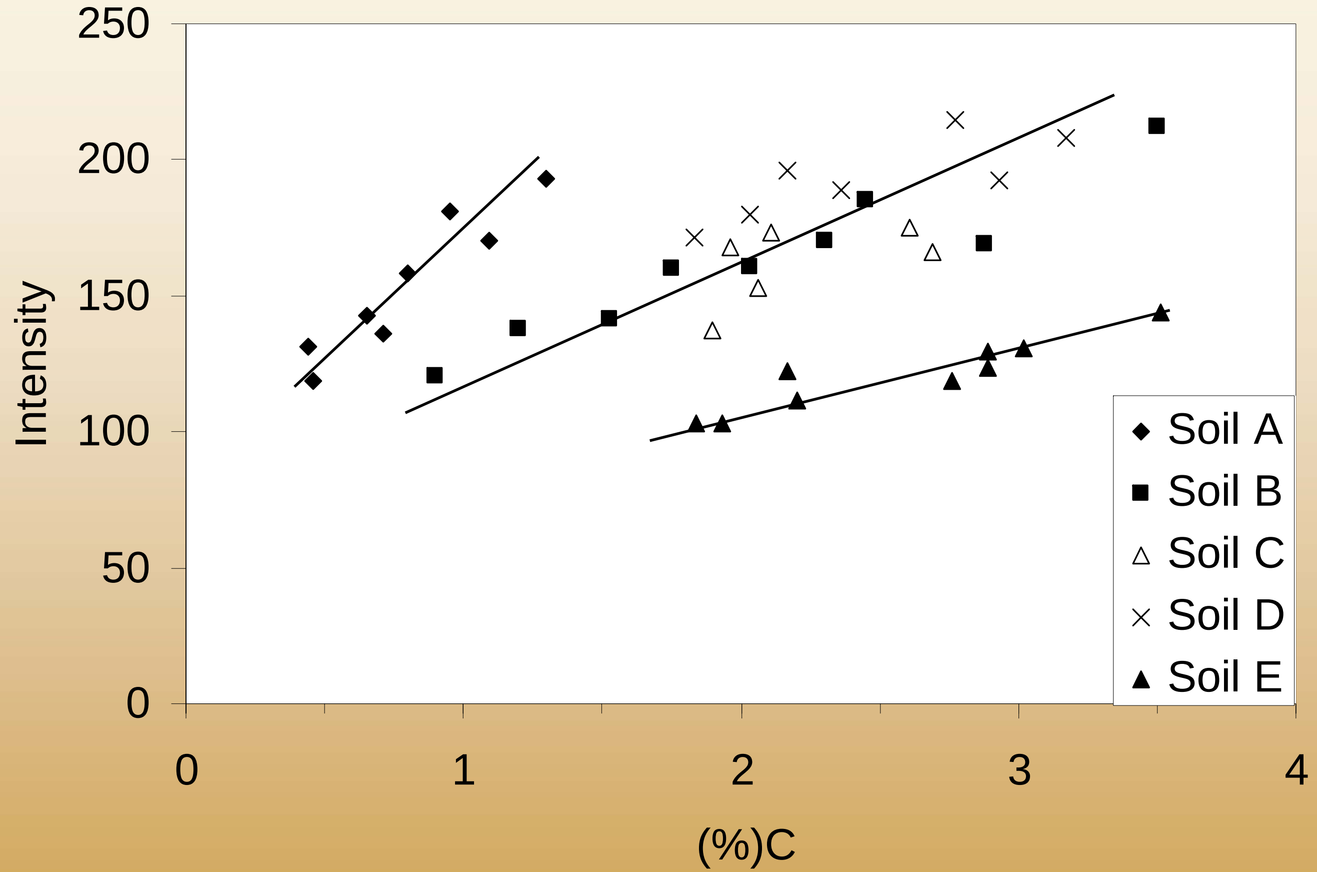
Cal Curves for Different Soil Types



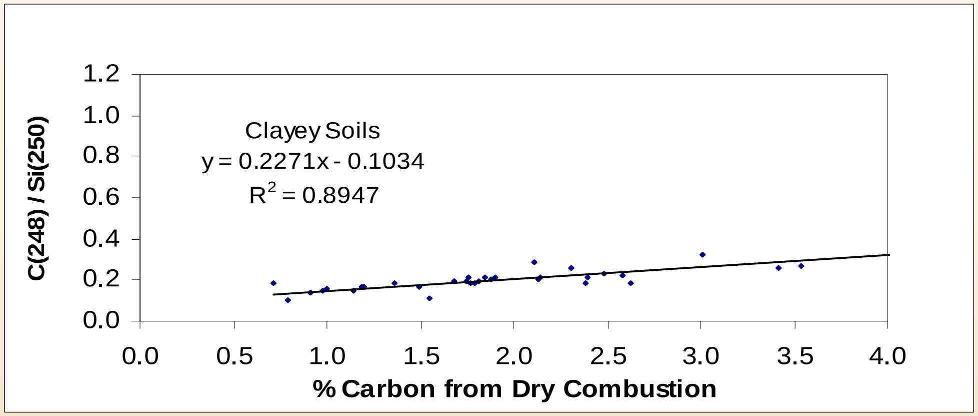
Soil A	Otley
Soil B	Vebar
Soil C	MICC17
Soil D	ILNL5
Soil E	MINC16

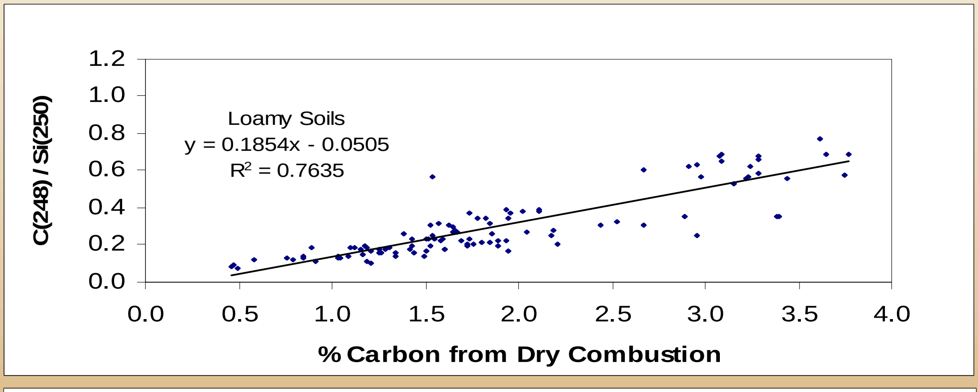
The slopes of the cal curves correlate with clay content of soil. Greater clay content produces less slope.

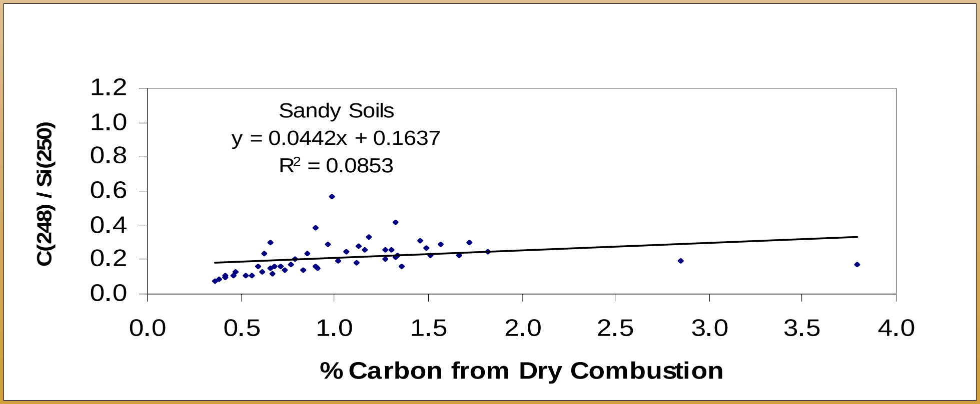
Soil Texture

- Best correlations obtained between LIBS and DC for finer textured soils
- As texture increases, the point detection characteristics of LIBS come into play
- The use of a long spark sampling method may alleviate this effect
- This is easily implemented on existing LIBS devices

NRCS soils group 2, DC %C vs LIBS C/Si, Soil Texture







Point spark

Long spark (≈100 greater area sampled)

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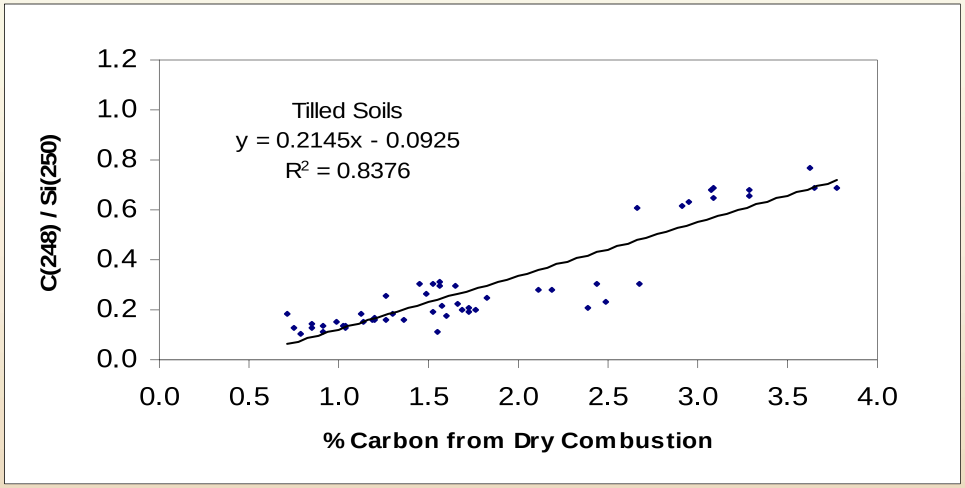
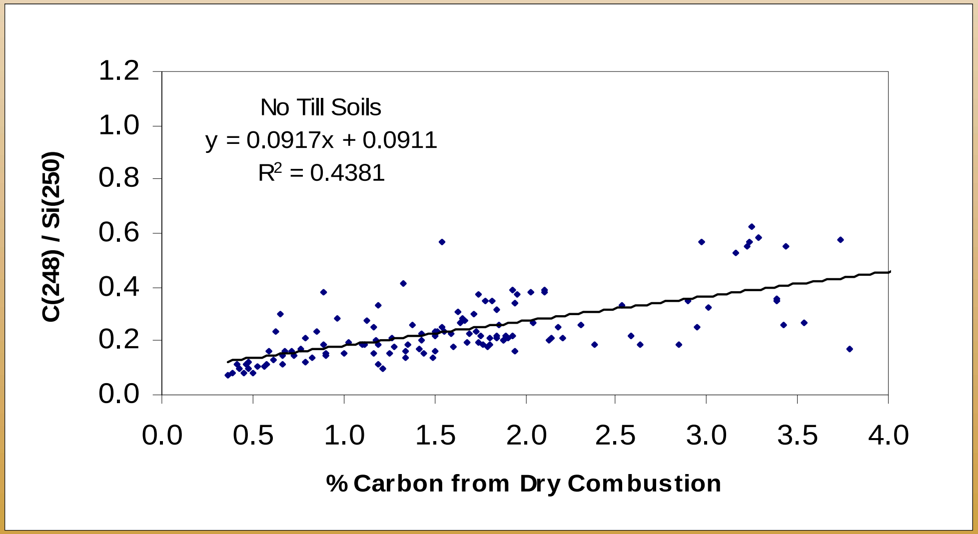
Effect of Tillage

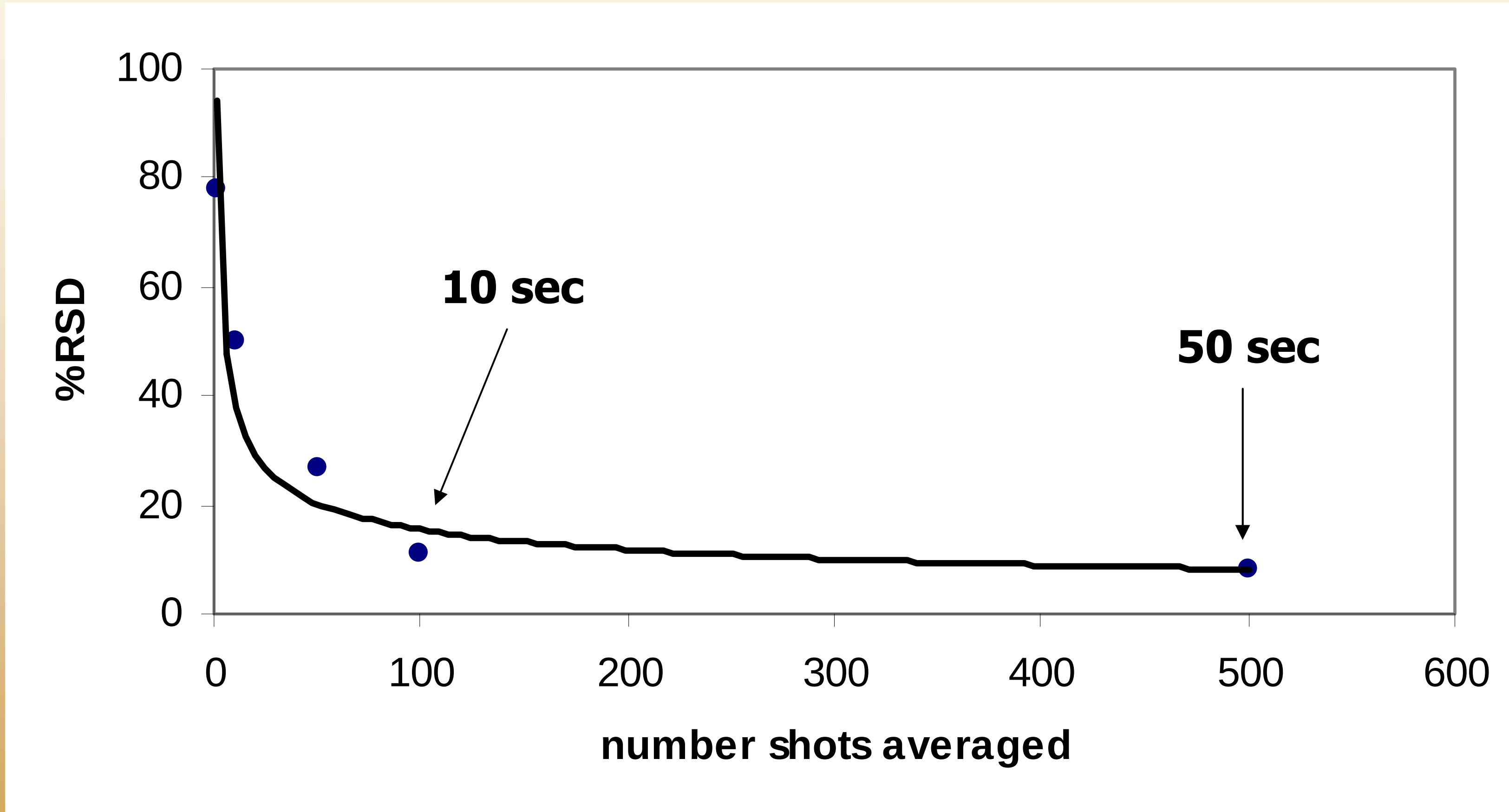
- Best correlations obtained between LIBS and DC for tilled soils
- Tillage increases carbon homogeneity in soil, the point detection characteristics of LIBS come into play here also
- This may be alleviated through the use of a long spark sampling method
- This is easily implemented on existing LIBS devices

NRCS soils group 2, DC %C vs LIBS C/Si, Till Effects





Effect of Spectra Averaged

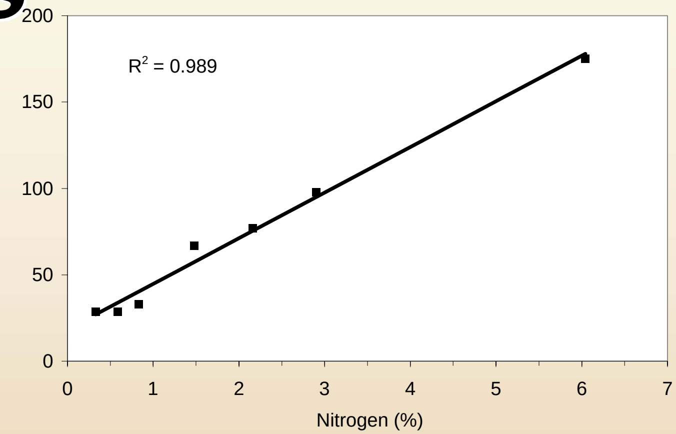


- **discrete soil sample**
- **sample moved under laser pulses**
- **10 Hz laser**

LIBS As a Soil Analysis Method

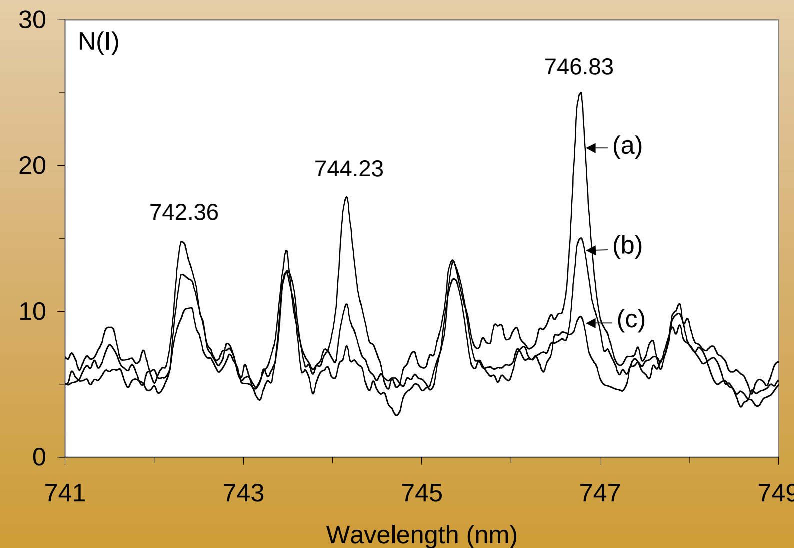
- LIBS provides rapid analysis of discrete soil and core samples
- Field & person-portable instruments developed and in testing
- Matrix effects for C detection have been identified and methods developed to minimize their effect
- Patents in preparation for instruments and matrix effects compensation
- Commercialization partners identified

Detection of Nitrogen in Soil by LIBS



Nitrogen calibration curve for spiked sea sand samples using N(I) 746.83 nm peak intensities.

- Detection of nitrogen in soil affected by atm. nitrogen (80% in air)
- By excluding air (0.04 Torr) nitrogen in soil can be detected
- Detection limit on order of 0.8% (by wt.)



Soil nitrogen monitored at reduced pressure (<40 mTorr) using neutral emission lines.

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LIBS has significant measurable data (science return) advantages over dry combustion for soil carbon analysis of core samples

➔ Within 15 minutes a 36-inch long core sample can be analyzed (120 separate measurements along the core) using LIBS

➔ This provides high resolution data on the carbon distribution in the most important top layers of soil

➔ A single measurement at a single point on the core using dry combustion will take at least 15 minutes

➔ In addition, LIBS can provide data on 20 or more other elements in the core simultaneous with the carbon measurement (may be useful with chemometrics to increase accuracy of carbon determination)

- **Data collection efficiency of LIBS for carbon alone is therefore ≈ 120 times greater**
- **Data collection efficiency of LIBS for carbon + 10 other elements is 2 x 120 = 240 times greater***

*** Assumes carbon is measured by dry combustion and other elements determined by another method such as x-ray fluorescence (assumes all other elements determined in 15 minutes)**

LIBS has several measurable cost advantages over dry combustion for soil carbon analysis for discrete samples

Steps in analysis procedure

start → result

Dry Combustion	Sample collection in the field	Transport to instrument in the lab	Sample preparation	Analysis
	2 minutes	Assume negligible cost - many samples can be transported simultaneously	30 minutes	10 minutes
LIBS*	2 minutes	Assume negligible cost	<1 minute	<1 minute
	Sample collection in the field**	Transport to instrument in the field	Sample preparation	Analysis

*** pertains to LIBS prototype in current testing program**

**** with fiber optic probe, sampling times will be reduced by a factor of ≈ 10**

- **Personnel cost efficiency of LIBS is therefore ≈ (2+30+10)/(2+1+1) = 10 times <u>greater</u>**
- **Estimated equipment operation costs (expendables, wear & tear):**

  LIBS: $0.10 per sample　　**Dry combustion: $0.50 per sample**
- **Overall cost efficiency: LIBS is (5 x 10) = 50 times more cost effective**

Fiber optic LIBS has several measurable time-saving advantages over dry combustion for soil carbon analysis for a discrete sample

start → Steps in analysis procedure → result

	Sample collection in the field	Transport to instrument in the lab	Sample preparation	Analysis
Dry Combustion	2 minutes	Hours/days	30 minutes	10 minutes
LIBS* w/fiber optic probe	12 seconds	none	none	<1 minute
	Fiber optic probe direct to soil	Transport to instrument in the field	Sample preparation	Analysis

Time efficiency of LIBS is therefore ≈ (2+120+30+10)/(0.2+0+0+1) = 135 times greater

*** Pertains to LIBS prototype in current testing program fitted with fiber optic probe**

Contributing Organizations

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